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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : B41M 5/28, 1/30, G03C 7/02

A1

(11) International Publication Number: WO 94/12352

(43) International Publication Date: 9 June 1994 (09.06.94)

(21) International Application Number: PCT/NL93/00250

(22) International Filing Date: 25 November 1993 (25.11.93)

(30) Priority Data:
9202096 2 December 1992 (02.12.92) NL

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(81) Designated States: AU, BB, BG, BR, BY, CA, CZ, FI, HU, JP, KP, KR, KZ, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: POLYMER COMPOSITION COMPRISING A POLYMER AND AT LEAST ONE RADIATION-SENSITIVE COMPONENT

(57) Abstract

The invention relates to a polymer composition comprising a polymer and a radiation sensitive substance, which can be modified by means of irradiation in such a way that after the irradiation the part of the surface of the polymer composition that has been subjected to irradiation has a colour that differs from the colour of the surface that has not been irradiated. The polymer composition according to the invention is characterized in that the radiation sensitive substance absorbs radiation in the visible range, the near infrared region and/or the near ultraviolet region can be modified in different ways, so that on the surface of the polymer composition several, mutually different chromatic colours can be obtained. It has been found that the polymer composition according to the invention can be irradiated in a simple way such that on the surface several, mutually different, chromatically coloured markings can be obtained. It also appears that the texture of the surface of the polymer composition does not change to the eye as a result of the irradiation. In specific cases the gloss of the surface shows no or hardly any change at the place of the irradiation. After the irradiation the markings on the surface appear to be very heat, weather and light resistant under conditions of use. It further appears that the markings are wear and scratch resistant, corrosion resistant, dimensionally stable, free of deformation and well legible. Finally, the physical and mechanical properties of the polymer composition are hardly or not at all affected by the application of the marking.

POLYMER COMPOSITION COMPRISING A POLYMER AND AT LEAST ONE RADIATION-SENSITIVE COMPONENT

The invention relates to a polymer composition comprising a polymer and at least one radiation sensitive substance, which can be modified by means of irradiation in such a way that after the irradiation the part of the surface of the polymer composition that has been subjected to irradiation has a colour that differs from the colour of the non-irradiated surface.

Such a polymer composition is known from patent application EP-A-327508. The polymer composition according to that patent application contains a radiation sensitive substance comprising at least one bleachable additive and at least one non-bleachable pigment. The polymer can be a thermoplastic as well as a thermosetting polymer. The bleachable additive is chosen from the group of indanthrone and azo pigments, while the non-bleachable pigment is chosen from the group of organic pigments, inorganic pigments and polymer-soluble colorants. On the surface of the polymer composition a marking is made by irradiating the surface of the polymer composition. A pulsed laser is used as radiation source. The wavelength of the laser light used is between 250 and 780 nm. After the irradiation the surface of the polymer composition shows a marking which has a colour that differs from the colour of the non-irradiated surface of the polymer composition. It is thus possible to make a marking, for instance as a decoration, an inscription or an indication, on the surface of the polymer composition according to EP-A-327508, in a colour which differs from that of the surface.

A disadvantage of the polymer composition described in EP-A-327508 is that only a marking of one chromatic colour differing from the colour of the surface

of the polymer composition can be obtained. In a number of applications, for instance in the case of a decoration or an indication, it is desirable, however, to have a marking of several colours differing from the colour of the non-irradiated surface of the polymer composition.

The objective of the present invention is the preparation of a polymer composition on which by means of irradiation a marking can be made of several chromatic colours that differ from each other as well as from the colour of the non-irradiated surface of the polymer composition.

The polymer composition according to the invention is characterized in that the radiation sensitive substance absorbs radiation in the visible range, the near infra-red region and/or the near ultra-violet region, can be modified in different ways, so that on the surface of the polymer composition several, mutually different chromatic colours can be obtained.

It has been found that the polymer composition according to the invention can be irradiated in a simple way such that on the surface several, mutually different, coloured markings can be obtained. It also appears that the texture of the surface of the polymer composition does not change visibly as a result of the irradiation. In specific cases the gloss of the surface shows no or hardly any change at the place of the irradiation. After the irradiation the markings on the surface appear to be very heat, weather and light resistant under conditions of use. It further appears that the markings are wear and scratch resistant, corrosion resistant, dimensionally stable, free of deformation and well legible. Finally, the physical and mechanical properties of the polymer composition are hardly or not at all affected by the application of a marking.

If an object scatters all the visible light between 400 and 700 nm, the colour of that object is white to the human eye. If, by contrast, all the visible light is absorbed, then the object is black. If part of each

wavelength of the visible light is absorbed, the object is grey. The colours white, grey and black are called 'achromatic colours'. In contrast to achromatic colours, chromatic colours are characterized by one or more absorption bands (absorption maxima and minima) in the visible range. If an absorption band lies between a wavelength of 400 and 430 nm, this means that that part of the incident light is absorbed. The rest of the incident light is scattered, so that the human eye perceives the object as yellow. In an analogous way, absorption bands at 430-480 nm, 480-550 nm, 550-600 nm and 600-700 nm give orange, red, violet and blue objects, respectively. The colour of an apparently green object is characterized by two absorption bands, one at 400-450 nm and one at 580-700 nm (see also Heinrich Zollinger, Color Chemistry, 1987, pp. 9-12, VCH Verlagsgesellschaft mbH, Weinheim, Germany).

The colour of an object may also be caused by reflection and/or emission of radiation of a certain wavelength. If radiation with a wavelength of between 600 and 700 nm is emitted, an object looks red. If for instance due to reflection in several layers certain wavelengths are extinguished as a result of interference, this will give the object a certain colour.

Colours have been standardized and defined in The Colour Index (1971-82), 3rd ed., Soc. Dyers Colourists, Bradford, and Am. Ass. Text. Chem. Colourists, Research Triangle Park, NC. In this standardization system, colours are defined by means of a C.I. number.

The radiation sensitive substance in the polymer composition according to the invention can be modified in several ways. In the context of the present invention, the modification of a substance is understood to mean the modification of a substance by means of irradiation in such a way that its colour changes, which is a consequence of the changing of the absorption spectrum or of the interference pattern of the substance at the place of the irradiation. It is possible that the radiation sensitive substance itself absorbs the radiation. It is also well

possible that another component in the polymer composition or the polymer matrix itself absorbs (part of) the radiation, after which the radiation sensitive substance is modified as a consequence of energy transfer (sensitization) or as a consequence of a chemical reaction. Preferably, the radiation sensitive substance itself absorbs the radiation.

In the context of the present invention, a radiation sensitive substance is understood to mean a substance which can be so modified by the effect of irradiation that the colour of the substance changes. This may mean that a colourless substance is modified to a coloured substance or that a coloured substance is removed or is modified to a colourless substance or that a coloured substance is modified to a differently coloured substance.

The radiation sensitive substance in the polymer composition can comprise several radiation sensitive components, but it is also possible that the radiation sensitive substance contains one radiation sensitive component which can be modified under several different irradiation conditions. This enables the surface of the polymer composition to be modified in such a way that a marking is obtained of several chromatic colours that differ from each other as well as from the colour of the non-irradiated surface.

The radiation sensitive substance comprises radiation sensitive components that can be chosen for instance from the group of organic and inorganic pigments, organic, inorganic and polymeric colorants, photochromic, thermochromic, piezochromic and prechromic compounds, coloured and uncoloured precursor colorants, coloured fillers, UV stabilizers, antioxidants, flame-retardants, acid formers, photooxidants and photoreductors. Optionally, a mixture of radiation sensitive components can be used. In a special embodiment of the invention the radiation sensitive components are wholly or partially bonded chemically or physically to the carrier material.

As carrier material can be used for instance polymers, dendritic macromolecules and zeolites. Preferably, the carrier material is porous.

The amount of radiation sensitive substance in the polymer composition according to the invention is mostly between 0.001 and 80 wt.%, preferably between 0.005 and 3 wt.% and more preferably between 0,01 and 1 wt.%. This percentage by weight is relative to the total weight of polymers and radiation sensitive substance.

Suitable radiation sensitive organic pigments are for instance acetylene black, aniline black, carbon black, animal charcoal, graphite and azo, azomethine, methine, anthrachinone, flavanthrone, phthalocyanine, indanthrone, pyranthrone, perinone, benzanthrone, perylene (for instance Pigment Red C.I. No. 224), dioxazine, thioindigo, triarylcarbonium, isoviolanthrone, anthanthron, antrapyrimidine, isoindoline (for instance Pigment Yellow C.I. No. 139), isoindolinone, chinacridone (for instance Pigment Violet C.I. No. 19), chinacridonchinone, benzimidazolone, ß-naphthol, pyrrolopyrrole and chinophthalone pigments. Also suitable are metal complexes of azo, azomethine, azopyridon and methine colorants, such as the azo condensation pigment Pigment Yellow C.I. No. 93 and the azo pigment Pigment Yellow C.I. No. 116. A survey of such pigments is given by Herbst and Hunger in Industrielle Organische Pigmente, VCH Verlagsgesellschaft, Weinheim (1987); see in particular pp. 583-624.

Examples of anthrachinone pigments are Pigment Red C.I. No. 177 and Pigment Yellow C.I. No. 147. An example of a flavanthrone pigment is Pigment Yellow C.I. No. 24. Examples of phthalocyanine pigments are Pigment Blue C.I. No. 15:3 and Pigment Green C.I. No. 7. An example of a perylene pigment is Pigment Red C.I. No. 149.

Suitable azo pigments for use as radiation sensitive component in the polymer composition according to the invention are for instance mono-, di-, tris- and multi-azo compounds derived from acetoacetarylide,

pyrazolone, 2,3-oxynaphthoic acid arylide, barbituric acid, thiobarbituric acid, 2,4,6-triamino-1,3-pyrimidine and 3-cyano-4-methylpyridone. Metal salts of azo compounds can also well be used as radiation sensitive component. Examples of highly suitable azo pigments are pigment Brown C.I. No. 23, Pigment Orange C.I. No. 31, Pigment Orange C.I. No. 60, Pigment Orange C.I. No. 64, Pigment Red C.I. No. 160, Pigment Red C.I. No. 220 and Pigment Red C.I. No. 221.

Suitable indanthrone pigments are for instance Cromophtal Blue A3R (Pigment Blue C.I. No. 60, Ciba-Geigy AG) and Pigment Blue C.I. No. 64.

Radiation sensitive inorganic pigments are for instance cobalt black, iron oxide (for instance Pigment Red C.I. No. 101), manganese dioxide, barium chromate, titanium dioxide (anatase, rutile), zinc oxide, antimony trioxide, zinc sulphide, lithophone, basic lead carbonate, basic lead sulphate, basic lead silicate, chromium oxide, nickel antimony titanate, chromium hydroxide, cobalt violet, cobalt yellow, iron cyanide blue, chromium antimony titanate, manganese blue, manganese violet, cobalt blue, cobalt chromium blue, cobalt nickel grey, ultramarine blue, ultramarine pink, ultramarine violet, vermilion, zinc chromate, zinc tetroxychromate, Berlin blue, lead chromate, lead sulphochromate, lead cyanamide, molybdenum chromate, nickel titanium yellow, strontium chromate, lead sulphochromate molybdate, molybdenum orange, molybdenum red (Pigment Red C.I. No. 104), cadmium sulphide, arsenic disulphide, antimony trisulphide, cadmium sulphoselenide, zirconium silicates, such as zirconium vanadium blue and zirconium praseodymium yellow.

Radiation sensitive polymer-soluble colorants are for instance anthrachinone compounds, such as hydroxy, amino, alkylamino, cyclohexylamino, arylamino, hydroxyamino and phenylmercapto anthrachinone, azo colorants, metal complexes of azo colorants, such as 1:2-chromium or cobalt complexes of mono-azo colorants, fluorescent colorants, such as compounds derived from

coumarin, naphthalimide, pyrazoline, acridine, xanthene, thioxanthene, oxazine, thiazine and benzothiazole, such as Solvent Yellow C.I. No. 163, Solvent Black C.I. No. 29 and Pigment Yellow C.I. No. 147.

The polymer-soluble colorants are mostly transparent and are preferably used in combination with fillers and/or pigments. More preferably, polymer-soluble colorants are used in combination with titanium dioxide.

Suitable precursor colorants and photochromic colorants are for instance spiropyran compounds, spirooxazine compounds, fulgides, dianthrylidene compounds, diarylethylene compounds, lactones, fluor anone, carbinol bases, styryl bases, cyanine bases and aromatic condensation products. Fulgides are described for instance in J. Chem. Soc. Perkin I, 1981, 197-201 (N.G. Heller). Diarylethylene compounds are described in J. Org. Chem., 1990, 55 2592-2596. Dianthrylidene compounds have been described by Fischer in Rev. of Chem. Intermediates, 1984, 5, 393-422. The spiropyran and spirooxazine compounds, the lactones, fluoranes, spirooxazine compounds, the lactones, fluoranes and bases have been described in Rev. Prog. Coloration, Vol. 19, 1989, 20-23, by Jones. Aromatic condensation products are described for instance in DE-A-4024647. Other aromatic condensation products are for instance oligomers of aniline or derivatives thereof.

Suitable thermochromic colorants are for instance fluorane compounds as described in Colourage, 1989, 36, 50-52, by N. Ayyangar.

Suitable piezochromic compounds have been described for instance in J. Chem. Physics, 1974, 64, 4567 ff. by Drickamer et al.

Suitable photooxidants are for instance chinone compounds, such as benzochinone and anthrachinone. Suitable photoreductors are for instance amino derivatives, such as hindered amine light stabilizers (HALS compounds) and N',N',N,N-tetramethyl-p-phenylene diamine.

Suitable acid formers are for instance isojodonium and sulphonium compounds as described for instance in Advances in Polymer Science 1984, <u>62</u> by Crivello et al. Also suitable are ester and amide compounds of sulphonic acids as described in Appl. Physics 189, <u>28</u>, p. 2126 by Yamaoka et al.

The radiation sensitive components, which can be modified under several different irradiation conditions, so that several chromatic colours can be obtained, are chosen for instance from the group of aromatic condensation products, such as for instance described in DE-A-4024647, oligomers of aniline or aniline derivatives, dianthrylidene compounds and lead sulphochromate molybdate.

Other suitable radiation sensitive components are for instance the so-called interference pigments. These pigments mostly contain platelet-shaped particles which absorb and/or transmit part of the incident light and reflect the rest so that a colour is perceived. These particles are described extensively in Kontakte (Darmstadt) 1992 (2), pp. 3-60 (Merck company).

Examples of such interference pigments are natural pearl essence (a mixture of guanine and hypoxanthine), lead carbonate, bismuth oxychloride and mica particles, which are in whole or in part provided with a metal oxide coating. Other platelet-shaped particles, for instance graphite, copper phthalocyanine, titanium dioxide and aluminium, coated with iron oxide, are also suitable for use as radiation sensitive component which can be modified under several different irradiation conditions, so that several chromatic colours can be obtained.

The mica particles are platelet-shaped particles which mostly have a thickness of between 300 and 600 nm and a length between 5 and 200 μm. The length preferably is between 5 and 40 μm. The metal oxide mostly is TiO_2 or Fe_2O_3. Depending on the thickness of the metal oxide coating, a certain colour is obtained. Mica particles

provided with a metal coating onto which a coating of TiO_2 has been applied are also suitable for use as radiation sensitive component. Such mica particles are described in EP-A-351932.

Optionally, the polymer composition according to the invention contains a coloured, radiation insensitive component. The radiation insensitive component is not modified under the irradiation conditions applied, and can consist of several different components. Examples of such radiation insensitive components are radiation insensitive, polymer soluble colorants and radiation insensitive organic and inorganic pigments.

The polymer in the polymer composition according to the invention can be chosen within wide limits; both natural and synthetic polymers are suitable. Depending on the envisaged application of the polymer, one skilled in the art can choose from the normally used groups of thermoplasts, thermosets, elastomers and biopolymers. Optionally, a mixture of polymers from several groups or a mixture of different polymers from a group is used.

Suitable thermoplastic polymers are for instance polyvinyl chloride or copolymers of vinyl chloride and other vinyl monomers, poly(vinylidene fluoride) or copolymers of vinylidene fluoride and other vinyl monomers, polystyrene or copolymers of vinyl aromatic monomers, such as styrene and α-methylstyrene, and other monomers, such as for instance maleic anhydride, acrylonitrile and maleimide, poly(meth)acrylates or copolymers of a (meth)acrylate with other monomers, poly(vinyl carbazole), polyolefins, such as for instance polyethylene, ultrahigh molecular weight polyethylene (UHMWPE), polyisobutylene, polybutene, poly(methyl pentene) and polypropylene, poly(vinyl acetate), poly(vinyl alcohol), polyacrylonitrile, poly((meth)acryl esters), polyamides, polyesters, such as for instance poly(ethylene terephthalate) and poly(butylene terephthalate), polycarbonates, poly(ether imides), poly(vinyl (m)ethyl ethers), poly(vinyl isobutyl ethers),

polyimides, polyethers, polysulphones, polyarylates, poly(ether sulphones), poly(ether esters), poly(phenylene oxides), poly(phenylene sulphides), poly(ester imides), poly(ether imides), polyurethanes, poly(amide imides), poly((m)ethylene oxides), polybutadiene rubbers, poly(tetrafluoro ethylene), acrylonitrile-butadiene-styrene copolymers, polyether-polyester block copolymers, liquid crystalline polymers and the like.

Suitable thermosetting polymers are for instance alkyd resins, polyester resins, amino resins, phenol resins, polyurethane resins, epoxy resins, silicone resins, ketone resins, melamine-urethane-formaldehyde resins, urethane-formaldehyde resins, melamine resins and acrylate resins.

Suitable elastomers are for instance ethene-propene copolymers, optionally containing a third comonomer, for instance dicylcopentadiene; cyclic rubbers, such as for instance polynorbornene; natural rubber, poly-butadiene, styrene-butadiene rubbers and norbornene-butadiene rubbers.

Suitable biopolymers are for instance polylactic acid, cellulose, cellulose nitrate, cellulose ester, cellulose triacetate, cellulose acetobutyrate, cellulose ether, (m)ethyl cellulose and benzyl cellulose.

The radiation sensitive components are mixed with the polymer to form the polymer composition according to the invention in a customary manner known to one skilled in the art. A roller, an extruder, an injection moulding machine or a mixing or grinding device can for instance be used for this purpose. It is also possible to mix the components into a solution, an emulsion or a suspension of the polymer, even during the polymerization of the polymer.

If it is desired to obtain an optimally homogeneous polymer composition, the radiation sensitive components should be dispersed as well as possible in the polymer. This has been described for instance by T.B. Reeve and W.L. Dills in 'Pigment Dispersion and Rheology

in Plastics', Pigment Handbook 1973, John Wiley & Sons, pp. 441-446. It is also well possible, however, to divide the radiation sensitive components inhomogeneously, which may result in great concentration differences in the polymer composition. This is the case for instance if the radiation sensitive components are localized selectively at the surface of the polymer composition, for instance by applying a multi-layer technique.

The pigments and colorants described can optionally be used with or without dispersion agents. Examples of suitable dispersion agents are fatty acids with at least 12 carbon atoms, for instance stearic acid, the amides, salts or esters of these fatty acids, for instance magnesium stearate, zinc stearate and aluminium stearate, quaternary ammonium compounds, for instance tri-(C1-C4)-alkyl benzyl ammonium salts, waxes, for instance polyethylene wax, resin acids, for instance abietic acid, rosin soap, hydrated or dimerized rosin, C12-C18 paraffin disulphonic acids and N-alkyl pyrrolidone compounds.

Optionally, fillers and/or antoxidants can be added to the polymer composition. Examples of fillers that can be added are chalk, talc, barium sulphate, fibres, kaolin, calcium carbonate, wollastonite, feldspar, aluminium silicate, calcite, dolomite and glass. Adhesion enhancement agents, flow-promoting agents, thickening agents, surface improvement agents, antifoaming agents, corrosion inhibitors, hardening agents, drying agents, conductive materials, such as conductive fibres and conductive flakes, mica, vulcanizing agents, peroxides, accelerators, stabilizers and binding agents can also be added.

The polymer composition obtained can be processed by the customary methods to the desired intermediate and/or final products. These products are mostly mouldings, such as films, sheets, tubes, profiles, plates, compression-moulded products or articles which are obtained by injection moulding, blow moulding, rotation moulding or RIM techniques. Further, in specific

applications the polymer composition according to the invention is excellently suitable for use as coating on a moulding.

In order to obtain on the surface of the polymer composition according to the invention or on the surface of a moulding that contains the polymer composition according to the invention a marking of a colour which differs from that of the surface, the surface is irradiated in such a way that at least one of the radiation sensitive components is wholly or partially modified. The marking obtained mostly has a thickness, measured from the surface of the polymer composition, between 0.1 and 1000 μm, preferably between 1 and 1000 μm, more preferably between 5 and 500 μm.

A suitable radiation source should emit radiation, for instance thermal or electromagnetic radiation, such as for instance light, of sufficient power to modify at least one of the radiation sensitive components.

Lasers are highly suitable for use as radiation source, but lamps, such as for instance IR lamps, UV lamps and VIS lamps, are good alternatives.

The polymer composition according to the invention can be irradiated from a stationary radiation source, if necessary with parts of the polymer composition screened off by means of a mask, or with a moving radiation source (writing or making discrete dots). It is also well possible to move the surface to be irradiated under a stationary radiation source. In this way the surface is also engraved by means of a writing technique as it were.

If a focused radiation beam is wanted, the emitted radiation can be bundled by means of a converging system of lenses. If a broad radiation beam is wanted, for instance if a mask is being used, the emitted radiation can be spread by means of a diverging system of lenses. In the case of a stationary radiation source, a radiation source of a large capacity is mostly used. In the case of

a moving, or writing, radiation source, a radiation source of a small capacity is mostly used. The writing speed of such a radiation source is mostly between 5 and 1000 mm/s, preferably between 15 and 500 mm/s, more preferably between 50 and 300 mm/s.

Examples of suitable radiation sources are gas lasers, such as for instance CO_2 lasers and N_2 lasers, excimer lasers, argon ion lasers, krypton ion lasers, diode lasers, copper vapour lasers, gold vapour lasers, manganese vapour lasers, lead vapour lasers, titanium sapphire lasers, ruby lasers, Alexandrite lasers, semiconductor lasers, Dye lasers and Neodymium Yttrium Aluminium Garnet (Nd:YAG lasers). Suitable radiation sources may emit a continuous beam of rays, but it is also possible to use a pulsating beam of rays. A survey of highly suitable lasers is given for instance by H. Hofmann in Proceedings of SPIE, The International Society for Optical Engineering, volume 744, 1987, pp. 156-180: 'Lasers in Motion for Industrial Applications'.

Suitable CO_2 lasers mostly emit light of a wavelength between 9 μm and 11 μm, preferably of about 10.6 μm (infrared).

Suitable Nd:YAG lasers emit light of a wavelength of 1064 nm; preferably, frequency doubling is applied, transforming the wavelength of the emitted light to 532 nm. The pulse energy applied is mostly between 0.01 and 100 J/cm^2, preferably between 1 and 20 J/cm^2 and more preferably between 1 and 10 J/cm^2; the peak load is about 40 MWatt. The pulse frequency mostly varies between 1 Hz and 10 kHz, preferably between 1 and 6 kHz. The pulse width mostly varies between 10^{-15} and 10^{-3} second, preferably between 10^{-12} - 10^{-6} second, most preferably between 10^{-6} - 10^{-7} second. The diameter of the parallel light beam mostly varies between 0.01 and 0.5 mm, preferably between 0.02 and 0.15 mm. The current strength applied is mostly between 10 and 25 A, preferably between 10 and 18 A, more preferably between 12 and 15 A. The energy density of the light beam applied is mostly between

0.10 $kWatt/cm^2$ and 1000 $GWatt/cm^2$

Suitable excimer lasers contain for instance xenon fluoride gas or xenon chloride gas and emit light of a wavelength of for instance 351 nm or 308 nm.

Suitable argon lasers emit light having wavelengths of for instance 514.5 nm, 502 nm, 496.5 nm, 488 nm, 476.5 nm and/or 458 nm, at a capacity of for instance 0.1 to 10 Watt. The capacity preferably is 1-5 Watt.

Lasers with accurately adjustable parameters, such as for instance the laser capacity and the wavelength, are preferred since they can be optimally adjusted to the specific process. The optimum laser parameters to be applied in marking the polymer composition according to the invention, which depend on the specific radiation sensitive component, can easily be set by one skilled in the art. The laser parameters should be set in a way that at least one of the radiation sensitive components is wholly or partially modified. Optionally, the laser parameters can be varied locally during the marking of the surface. Examples of such parameters are the radiation load, the radiation intensity, the pulse mode, the pulse width, the pulse sequence, the writing speed and the wavelength.

Optionally, (part of) the surface of the polymer composition is irradiated sequentially, with one or more laser parameters being varied.

During the irradiation of the surface of the polymer composition according to the invention or of a moulding comprising the polymer composition according to the invention, at least one of the radiation sensitive components is wholly or partially modified. By this is understood that a colourless component is wholly or partially modified to a coloured component, or that a coloured component is wholly or partially removed or wholly or partially modified to a colourless component (for instance by bleaching it) or that a coloured component is wholly or partially modified to a differently

coloured component.

Optionally, part of the surface of the polymer composition is molten, carbonized or foamed during the irradiation. It is also possible to cause a radiation sensitive component to be wholly or partially disintegrated during the irradiation, so that the radiation sensitive component is redispersed. This can result in a change of colour.

After irradiation of the surface of the polymer composition according to the invention a moulding is obtained whose surface is provided with at least one marking of a chromatic colour that contrasts with the colour of the non-irradiated surface. If the radiation sensitive component has been modified in several ways, the surface of the moulding can have at least two different chromatic colours differing from the colour of the non-irradiated surface, which can moreover be different from each other.

After the irradiation of the surface, the texture of the surface of the moulding may have slightly changed. Preferably, the texture of the surface at the place of the irradiation is not essentially different from the texture of the non-irradiated surface.

The invention will be further elucidated by means of the following non-restrictive examples.

Examples

Example I

98.74 parts by weight (w/w%) polybutylene terephthalate (Arnite TV4 261, DSM, dried for 4 hours at 140°C and reduced pressure) were dry-coated with 0.03 w/w% Paliogen Red K 3911 HD (perylene type pigment, pigment red 178, BASF), 0.75 w/w% Meteor Plus Teal Blue (Co/Ti oxide, pigment green 50, Engelhard), 0.03 w/w% PV Echtgelb HG (mono-azo pigment, pigment yellow 180, Hoechst), 0.30 w/w% Kronos CL 220 (TiO_2) pigment white 6, Kronos) and 0.15

w/w% Mg stearate. The resulting mixture was injection-moulded to moss-grey platelets (90 * 80 * 2 mm) using an Arburg Allrounder (220-90-350) injection moulding machine equipped with a D&L screw (22 mm) and having a cylinder temperature of 260°C.

Next, the platelets were engraved using an SHG Nd:YAG Q-switch laser (pulse time 110 ns, 532 nm, Haas Laser 6411 Engraving System, Haas Laser) both with low (about 2 J/cm^2) and high (about 6 J/cm^2) laser beam intensity. With low intensity a pink-red marking was obtained, while with high intensity the marking was of a grey-green colour. In this way platelets with markings in two colours were obtained. In both cases the texture of the surface was not visibly changed.

Example II

99.50 w/w% polymethylene oxide (Ultraform N2230, BASF, dried for 2 hours at 80°C) were dry-coated with 0.20 w/w% Horna Orange MLH-84-SQ (lead sulphochromate molybdate, pigment red 104, Ciba-Geigy), 0.20 w/w% Chromoxidgrün GN-M(Cr_2O_3, pigment green 17, Bayer), 0.05 w/w% Macrolex Yellow 6G (disperse yellow 201, Bayer) and 0.05 w/w% Mg stearate. The resulting mixture was injection-moulded to ochre-brown platelets (90 * 80 * 2 mm) at a cylinder temperature of 180°C on a Netstal Neomat 350/130 injection moulding machine, equipped with a standard screw and a Twente mixing ring injection nozzle. Next, one platelet was engraved using an SHG Nd:YAG Q-switch laser (pulse time 110 ns, 532 nm, Haas Laser 6411 Engraving System, Haas Laser) both with low (about 2 J/cm^2) and high (about 6 J/cm^2) laser beam intensity. With low intensity a yellow-green marking was obtained, while with high intensity the marking was of a fern-green colour. In this way a platelet with markings in two colours was obtained. In both cases the texture of the surface was not visibly changed. A second platelet was engraved using an SHG Nd:YAG Q-switch laser (pulse time 110 ns, 532 nm, Haas Laser 6411 Engraving System, Haas

Laser) with low (about 2 J/cm^2) intensity. When a part of the resulting yellow-green marking was next irradiated with the light from a high-pressure mercury lamp, it turned to a fern-green colour. With this procedure as well, a platelet was obtained with markings in two colours. The texture of the surface was not visibly changed either in this case.

Example III

99.50 w/w% acrylonitrile-butadiene-styrene copolymer (Ronfalin FG50, DSM, dried for 2 hours at 80°C) were dry-coated with 0.50 w/w% Horna Orange MLH-84-SQ (lead sulphochromate molybdate, pigment red 104, Ciba-Geigy). The resulting mixture was injection-moulded to orange-pink platelets (65 * 65 * 3 mm) using an Arburg Allrounder (220-90-350) injection moulding machine equipped with a D&L screw (22 mm) and having a cylinder temperature of 240°C. Next, a part of a platelet thus obtained was engraved using an SHG Nd:YAG Q-switch laser (pulse time 110 ns, 532 nm, Haas Laser 6411 Engraving System, Haas Laser) with low (about 2 J/cm^2) intensity. The resulting marking had a pastel-yellow colour. Another part of the injection-moulded platelet was engraved with a high-intensity laser beam (about 6 J/cm^2). The resulting marking was of an ochre-brown colour. In this way a platelet with markings in two colours was obtained. In both cases the texture of the surface was not visibly changed.

Example IV

99.50 w/w% polycarbonate (Xantar 24R, DSM, dried for 5 hours at 120°C) were dry-coated with 0.50 w/w% Horna Orange MLH-84-SQ (lead sulphochromate molybdate, pigment red 104, Ciba-Geigy). The resulting mixture was injection-moulded to vermilion-red platelets (65 * 65 * 3 mm) using an Arburg Allrounder (220-90-350) injection moulding machine equipped with a D&L screw (22 mm) and having a cylinder temperature of 300°C. Next, a part of a platelet

thus obtained was engraved using an SHG Nd:YAG Q-switch laser (pulse time 110 ns, 532 nm, Haas Laser 6411 Engraving System, Haas Laser) with low (about 2 J/cm^2) intensity. The resulting marking had an orange-brown colour. Another part of the injection-moulded platelet was engraved with a high-intensity laser beam (about 6 J/cm^2). The resulting marking was of a loam-brown colour. A part of this loam-brown marking was once more engraved with the high-intensity laser beam. This part of the marking had an olive-brown colour. In this way a platelet with markings in three colours was obtained. The texture of the surface was not visibly changed.

Example V

76.77 w/w% polypropylene (Stamylan PP 48MN40, DSM) were kneaded for 15 minutes at 200°C on a Haake kneader with 6.90 w/w% Cromophtal Violet B (dioxazine pigment, pigment violet 34, Ciba Geigy), 2.30 w/w% Cromophtal Yellow 3G (diazo condensation pigment, pigment yellow 93, Ciba Geigy) and 14.03 w/w% Kronos CL 220 (TiO_2, pigment white 6, Kronos). The masterbatch thus obtained was next processed to granulate. A part of the masterbatch granulate was mixed with virgin polypropylene granulate in a ratio of 1:23, after which the resulting mixture was injection-moulded to red-mauve platelets (90 * 80 * 2 mm) using an Arburg Allrounder (220-90-350) injection moulding machine equipped with a D&L screw (22 mm) and having a cylinder temperature of 240°C.

Next, a part of a platelet thus obtained was engraved using an SHG Nd:YAG Q-switch laser (pulse time 110 ns, 532 nm, Haas Laser 6411 Engraving System, Haas Laser) with low (about 2 J/cm^2) intensity. The resulting marking had a grey-blue colour. Another part of the injection-moulded platelet was engraved with a high-intensity laser beam (about 6 J/cm^2). The resulting marking was of reseda-green colour. In this way a platelet with markings in two colours was obtained. In both cases the texture of the surface was not visibly changed.

Example VI

98.21% w/w% acrylonitrile-butadiene-styrene (Ronfalin FG-50, DSM) were dry-coated with 0.45 w/w% Kronos CL 220 (TiO_2, pigment white 6, Kronos), 0.62 w/w% Bayferrox 130 BM (Fe_2O_3, pigment red 101, Bayer), 0.18 w/w% Cromophtal Blue A3R (indanthrone pigment, pigment blue 60, Ciba-Geigy), 0.09 w/w% Sandorin Green 3 GLSP (halogenated Cu phthalocyanine pigment, pigment green 7, Sandoz) and 0.45 w/w% Mg stearate. The resulting mixture was injection-moulded to purple-mauve platelets (90 * 80 * 2 mm) using an Arburg Allrounder (220-90-350) injection moulding machine equipped with a D&L screw (22 mm) and having a cylinder temperature of 240°C. Next, a part of a platelet thus obtained was engraved using an SHG Nd:YAG Q-switch laser (pulse time 110 ns, 532 nm, Haas Laser 6411 Engraving System, Haas Laser) with a low-intensity laser beam (about 2 J/cm^2). The resulting marking had a cobalt-blue colour. The texture of the surface was not visibly changed. A second part of the injection-moulded platelet was engraved with a high-intensity laser beam (about 6 J/cm^2). The surface melted and assumed a pale-green colour. A third part of the platelet was irradiated with an SHG Nd:YAG Q-switch laser (1064 nm, Haas Laser 6211 Engraving System, Haas Laser) and turned concrete-grey, while the surface was foamed.

Example VII

91.50 w/w% acrylonitrile-butadiene-styrene (Ronfalin SFB 34, DSM, dried for 2 hours at 80°C) were dry-coated with 0.20 w/w% Irgalite Blue LGLD (Cu phthalocyanine (ß) pigment, pigment blue 15:3, Ciba Geigy), 0.20 w/w% Cromophtal Red G (diazo condensation pigment, pigment red 220, Ciba Geigy) and 8.10 w/w% Kronos CL 220 (TiO_2, pigment white 6, Kronos). The resulting mixture was injection-moulded to lilac-grey platelets (90 * 80 * 2 mm) using an Arburg Allrounder (220-90-350) injection moulding machine equipped with a D&L screw (22 mm) and having a cylinder temperature of 220°C. Next, a

part of a platelet thus obtained was engraved using an SHG Nd:YAG Q-switch laser (pulse time 110 ns, 532 nm, Haas Laser 6411 Engraving System, Haas Laser) with a high-intensity laser beam (about 6 J/cm^2). The surface melted and got a pale-green colour. The marking obtained appeared to be scratch resistant and light resistant. Another part of the injection-moulded platelet was engraved using an SHG Nd:YAG Q-switch laser (pulse time 10 ns, 532 nm, Quanta Ray DCR 2, Spectra Physics), which resulted in a light-blue marking and did not bring about a visible change in the texture of the surface.

Example VIII

Example VII was repeated, using only 0.80 w/w% Kronos CL 220 (TiO_2, pigment white 6, Kronos). Mauve-blue platelets were now obtained. Next, a part of an injection-moulded platelet thus obtained was engraved using an SHG Nd:YAG Q-switch laser (pulse time 110 ns, 532 nm, Haas Laser 6411 Engraving System, Haas Laser) with a high-intensity laser beam (about 6 J/cm^2), which caused the surface to melt and resulted in a turquoise marking. Irradiation with low intensity (about 2 J/cm^2) at another spot of the platelet resulted in a dark-blue marking, without causing a change in the texture of the surface. Parts of the platelet thus irradiated were subsequently irradiated for 2 to 24 hours by means of an unfiltered high-pressure mercury lamp. With increasing irradiation time, the dark-blue marking progressively became light-blue.

Example IX

200 grammes of polymethyl methacrylate (PMMA, Oroglas V 052, Rohm & Haas) were dissolved in 1 litre of methyl ethyl ketone (MEK). To 20 grammes of the resulting solution were added 28 mg Bayferrox 130 BM (Fe_2O_3, pigment red 101, Bayer), 9 mg PV Echtgelb HG (mono-azo pigment, pigment yellow 180, Hoechst), 33 mg Ultramarine Blue RS 6 (Na silicate, pigment blue 29, Reckitt's) and 130 mg CL

Kronos 220 (TiO_2, pigment white 6, Kronos). The resulting solution was mixed ultrasonically for two minutes and then poured out. After drying a glossy, light-brown film was obtained. Next, a part of the film thus obtained was engraved using an SHG Nd:YAG Q-switch laser (pulse time 110 ns, 532 nm, Haas Laser 6411 Engraving System, Haas Laser) with low (about 2 J/cm^2) intensity. The resulting marking had a reseda-green colour. Another part of the film was engraved with a high-intensity laser beam (about 6 J/cm^2). The resulting marking was of a light-yellow colour. In both cases the texture of the surface was not visibly changed.

Example X

200 parts by weight of a saturated melamine-formaldehyde polyester resin were mixed with 15 parts by weight of a pigment composition, using 100 g of glass beads (d = 1 mm). The pigment composition consisted of 20 parts by weight of Microlith-WA White R-WO (TiO_2, pigment white 6, Ciba Geigy), 1 part by weight of Microlith-WA Black C-WA (carbon black, pigment black 7, Ciba Geigy), 2 parts by weight of Bayferrox 130 BM (Fe_2O_3, pigment red 101, Bayer), 2 parts by weight of Cromophtal Blue A3R (indanthrone pigment, pigment blue 60, Ciba-Geigy) and 1 part by weight of Irgalite Yellow F4G (arylamide pigment, pigment yellow 111, Ciba Geigy). The brown paint thus obtained was sprayed onto aluminium plates, after which the painted plates were cured in the air for 15-20 minutes at a temperature of 150°C. Next, a part of a painted plate thus obtained was engraved using an SHG Nd:YAG Q-switch laser (pulse time 110 ns, 532 nm, Haas Laser 6411 Engraving System, Haas Laser) with low (about 2 J/cm^2) intensity. The resulting marking had a dark-green colour. Another part of the painted plate was engraved with a high-intensity laser beam (about 6 J/cm^2). The resulting marking was of a light-yellow colour. In both cases the texture of the surface was not visibly changed. Next, another part of the painted plate was engraved using an

SHG Nd:YAG Q-Switch laser (1064 nm, Haas Laser 6211 Engraving System, Haas Laser). This resulted in a grey-blue marking, with some roughening of the surface. The markings can be applied without affecting the adhesive power of the paint to the plate.

Example XI

Analogously to example X, a resin mixture was prepared, the pigment composition consisting of 20 parts by weight of Microlith-WA White R-WO (TiO_2, pigment white 6, Ciba Geigy), 1 part by weight of Microlith-WA Black C-WA (carbon black, pigment black 7, Ciba Geigy), 2 parts by weight of Bayferrox 130 BM (Fe_2O_3, pigment red 101, Bayer), 2 parts by weight of Cromophtal Blue A3R (indanthrone pigment, pigment blue 60, Ciba Geigy) and 1 part by weight of Macrolex Orange 3G (perinone pigment, solvent orange 60, Bayer). Next, part of a mauve-blue plate obtained was engraved using an SHG Nd:YAG Q-switch laser (pulse time 110 ns, 532 nm, Haas Laser 6411 Engraving System, Haas Laser) with low (about 2 J/cm^2) intensity. The resulting marking had a dark-blue colour. Another part of the painted plate was engraved with a high-intensity laser beam (about 6 J/cm^2). The resulting marking was of a light-blue colour. In both cases the texture of the surface was not visibly changed. As a function of the laser intensity applied, it appeared to be possible to obtain each shade of blue between said two extremes. Next, another part of the painted plate was engraved using an SHG Nd:YAG Q-Switch laser (1064 nm, Haas Laser 6211 Engraving System, Haas Laser). This resulted in a grey-blue marking, with some foaming.

Example XII

Example X was repeated, but now using the following pigment composition: 1 part by weight of Iriodine 9505 red violet (metal oxide coated mica particles, Merck) and 1 part by weight of Iriodine 111 Rutile Fine Satin (TiO_2-coated mica particles, Merck). The

paint thus obtained was sprayed onto a black ABS plate. Next, a part of the resulting bordeaux-coloured plate was engraved using an SHG Nd:YAG Q-switch laser (pulse time 110 ns, 532 nm, Haas Laser 6411 Engraving System, Haas Laser) with low (about 2 J/cm^2) intensity. The resulting marking had an ultramarine blue colour. Another part of the painted plate was engraved with a high-intensity laser bundle (about 6 J/cm^2). The marking obtained was of a pastel turquoise colour. In both cases the texture of the surface was not visibly changed. As a function of the laser intensity applied, it appeared to be possible to obtain each shade of blue between said two extremes. Irradiation of the surface with an intensity of 10 J/m^2 resulted in a white marking, with some roughening of the surface.

<u>Example XIII</u>

99.06 w/w% polymethylene oxide (Ultraform N2230, BASF, dried for 2 hours at 80°C) were dry-coated with 0.50 w/w% Meteor Plus Teal Blue (TiO_2/CoO, pigment green 50, Engelhard), 0.02 w/w% Paliogen Red K3911 HD (perylene pigment, pigment red 178, BASF), 0.02 w/w% PV Echtgelb HG (benzimidalone pigment, pigment yellow 180, Hoechst), 0.30 w/w% Kronos CL 220 (TiO_2, pigment white 6, Kronos) and 0.10 w/w% Mg stearate. The resulting mixture was injection moulded to olive-green platelets (90 * 80 * 2 mm) at a cylinder temperature of 180°C on a Netstal Neomat 350/130 injection moulding machine, equipped with a standard screw and a Twente mixing ring injection nozzle. Next, a part of a platelet was engraved using an SHG Nd:YAG Q-switch laser (pulse time 110 ns, 532 nm, Haas Laser 6411 Engraving System, Haas Laser) with the laser beam on high intensity (about 6 J/cm^2). This resulted in a cyane-coloured marking, with no visible change in the texture of the surface. At low intensity, the red pigment present was redispersed and a pink-red marking resulted. The texture of the surface of the markings obtained was not visibly changed. A second platelet was engraved using an SHG

Nd:YAG Q-Switch laser (1064 nm, Haas Laser Engraving System, Haas Laser). This resulted in a silver-coloured marking, with some foaming of the surface.

Example XIV

98.53 w/w% polycarbonate (Xantar 24R, DSM) were dry-coated with 0.47 w/w% Tiofine R41 (TiO_2, pigment white 6, Tiofine), 0.33 w/w% Bayferrox 130 BM (Fe_2O_3, pigment red 101, Bayer), 0.67 w/w% mg Ultramarine Blue RS6 (Na silicate, pigment blue 29, Reckitt's) and 0.20 w/w% Printex 85 (carbon black, pigment black 7, Degussa). The resulting mixture was injection-moulded to black platelets (90 * 80 * 2 mm) using an Arburg Allrounder (220-90-350) injection moulding machine equipped with a D&L screw (22 mm) and having a cylinder temperature of 280°C. A part of the platelet was engraved using an SHG Nd:YAG Q-Switch laser (1064 nm, Haas Laser 6211 Engraving System, Haas Laser), which resulted in a red-mauve marking. A part of the red-mauve marking was then engraved using an SHG Nd:YAG Q-switch laser (pulse time 110 ns, 532 nm, Haas Laser 6411 Engraving System, Haas Laser) with high intensity (about 6 J/cm^2). This resulted in a bright blue marking.

Example XV

200 grammes of polymethyl methacrylate (Oroglas V052, Rohm & Haas) were dissolved in 1 litre of methyl ethyl ketone. To 20 grammes of this solution were added 100 mg of N,N,N'N'-(tetramethyl)-p-phenylene diamine (Aldrich) and 100 mg of trismesyl ester of 1,3,5-tris-hydroxybenzene. Next, the resulting mixture was mixed ultrasonically for two minutes, poured out and dried. This resulted in a transparent, uncoloured film. A part of the film was exposed to a CW Rayonet lamp (254 nm), which resulted in a light-yellow marking. Another part of the film was irradiated with an excimer laser (308 nm, LPX 200, Lambda Physics), which resulted in a dark-blue marking. The texture of the surface of the markings

obtained was not visibly changed.

Example XVI

99.50 w/w% ABS granulate (Ronfalin FG-50, DSM) was dry-coated with 0.50 w/w% HORNA Orange MLH-84-SQ (lead sulphochromate molybdate, pigment red 104, Ciba Geigy). On an Arburg Allrounder (220-90-350) equipped with a D&L screw (ø 22 mm) and having a cylinder temperature of 240°C, this was injection moulded to test bars for mechanical measurements.

Part of these test bars were engraved with an SHG Nd:YAG Q-switch laser (532 nm, Haas Laser Engraving System, Haas Laser), which resulted in a yellow marking without disturbing the surface. This yellow marking was applied both on one side and on two sides of the bars. Several mechanical tests were performed on these bars, viz. tensile strength test, flexural strength test, Izod impact test and Charpy impact test.

Results of tensile strength test (average of 5 measurements) (according to DIN 53455)

	E-modulus [MPa]	Tensile stress at yield [MPa]	Tensile stress at break [MPa]	Elongation at break [%]
Unmarked	2332±19	44.9±0.3	28.3±4.8	10.7±2.4
Single marking	2343±30	44.8±0.4	28.3±5.2	12.5±4.0
Double marking	2320±19	44.9±0.1	26.6±3.2	10.6±1.8

Results of flexural strength test (according to DIN 53452)

	E-modulus [MPa]	Maximum bending stress [MPa]
Unmarked	2636±23	76.6±0.2
Single marking	2619±7	76.4±0.1
Double marking	2641±17	76.7±0.2

Results of Izod impact test (according to DIN 51230)

	Impact resistance [kJ/m^2]
Unmarked	18.2±0.2
Single marking	18.3±0.3
Double marking	19.0±0.7

Results of Charpy impact test (-40°C) (according to DIN 53453)

	Impact resistance [kJ/m^2]
Unmarked	75.0±21.3
Single marking	58.0±4.5
Double marking	60.5±6.6

From the experiments it appears that the mechanical properties of the polymer are not affected by the laser marking.

Example XVII

Analogously to example XVI, PC (Xantar 24R, DSM) test bars were made at a cylinder temperature of 280°C. Analogously to example XVIII these were marked or not marked. Several mechanical tests were performed on these bars, viz. tensile strength test, flexural strength test and Izod impact test.

Results of tensile strength test (average of 5 measurements) (according to DIN 53455)

	E-modulus [MPa]	Tensile stress at yield [MPa]	Tensile stress at break [MPa]	Elongation at break [%]
Unmarked	2346±23	59.4±0.2	66.1±2.2	112.8±4.6
Single marking	2349±14	59.4±0.2	66.6±2.3	119.9±5.4
Double marking	2367±29	59.2±0.2	61.3±6.9	100.4±17.8

Results of flexural strength test (according to DIN 53452)

	E-modulus [MPa]	Maximum bending stress [MPa]
Unmarked	2622±20	106.5±0.5
Single marking	2611±23	106.4±0.8
Double marking	2622±33	105.5±0.7

Results of Izod impact test (according to DIN 51230)

	Impact resistance [kJ/m²]
Unmarked	12.0±3.3
Single marking	13.1±3.2
Double marking	11.0±0.8

From these experiments as well it appears that the mechanical properties of the polymer are not affected by the laser marking.

CLAIMS

1. Polymer composition comprising a polymer and a radiation sensitive substance, which can be modified by means of irradiation in such a way that after the irradiation the part of the surface of the polymer composition that has been subjected to irradiation has a colour that differs from the colour of the surface, characterized in that the radiation sensitive substance absorbs radiation in the visible range, the near infra-red region and/or the near ultra-violet region, can be modified in different ways, so that on the surface of the polymer composition several, mutually different chromatic colours can be obtained.
2. Polymer composition according to claim 1, characterized in that the radiation sensitive substance comprises at least one radiation sensitive component which can be modified under at least two different irradiation conditions.
3. Polymer composition according to any one of claims 1-2, characterized in that the radiation sensitive substance contains at least two different radiation sensitive components.
4. Polymer composition according to any one of claims 1-3, characterized in that the radiation sensitive component is chosen from the group of organic and inorganic pigments, organic, inorganic and polymeric colorants, photochromic, thermochromic and prechromic compounds, coloured and uncoloured precursor colorants, coloured fillers, UV stabilizers, antioxidants, flame-retardants, acid formers, photooxidants and photoreductors.
5. Polymer composition according to any one of claims 1-4, characterized in that the radiation sensitive component is chosen from the group of aromatic condensation products of naphthalene and perylene, aniline and aniline derivatives, helianthrone

compounds and lead sulphochromate molybdate.

6. Polymer composition according to any one of claims 1-5, characterized in that the polymer composition contains plate-shaped particles chosen from the group of natural pearl essence, lead carbonate, bismuth oxychloride, mica particles wholly or partly coated with metal oxide; graphite, copper phthalocyanine, titanium dioxide, and aluminium coated with iron oxide.

7. Polymer composition according to claim 6, characterized in that the plate-shaped particles are mica particles having a thickness of between 300 and 600 nm and a length of between 5 and 200 μm.

8. Polymer composition according to claim 6 or 7, characterized in that the plate-shaped particles are at least partly coated with a radiation sensitive component.

9. Polymer composition according to claim 8, characterized in that the radiation sensitive component contains TiO_2 and/or Fe_2O_3.

10. Polymer composition according to any one of claims 1-9, characterized in that the radiation sensitive substance comprises one or more organic or inorganic pigments.

11. Polymer composition according to claim 10, characterized in that the organic or inorganic pigments are chosen from the group of azo pigments, azo colorants, metal complexes of azo compounds, Fe_2O_3, dioxazine pigments and carbon black.

12. Polymer composition according to any one of claims 1-11, characterized in that the radiation sensitive substance comprises one or more non-colour-forming components which are colour forming after modification.

13. Polymer composition according to claim 12, characterized in that the non-colour-forming component is chosen from the group of dianthrylidene compounds, aromatic condensation products of

naphthalene and perylene, cyanine phthalides, fluorans and spiropyran compounds.

14. Polymer composition according to any one of claims 1-13, characterized in that the weight percentage of radiation sensitive substance in the polymer composition is 0.001-80, relative to the total weight of polymer and radiation sensitive substance.

15. Polymer composition according to any one of claims 1-14, characterized in that the polymer composition contains a radiation insensitive substance.

16. Polymer composition according to any one of claims 1-15, characterized in that the polymer is a thermoplastic polymer.

17. Polymer composition according to claim 16, characterized in that the thermoplastic polymer is chosen from the group of polyolefins, polyoxides, polyesters, polystyrene, acrylonitrile-butadiene-styrene, polyamide and polycarbonate.

18. Polymer composition according to any one of claims 1-17, characterized in that the polymer is a thermosetting polymer.

19. Polymer composition according to claim 18, characterized in that the thermosetting polymer is chosen from the group of alkyd resins, polyester resins, amino resins, phenol resins, polyurethane resins, epoxy resins, melamine-urethane-formaldehyde resins, urethane-formaldehyde resins, melamine resins and acrylate resins.

20. Process for marking a polymer composition according to any one of claims 1-19, characterized in that the surface of the polymer composition is irradiated in such a way that at least one of the radiation sensitive components in the polymer composition is wholly or partially modified and the surface of the polymer composition changes in colour at the place of the irradiation.

21. Process according to claim 20, characterized in that the surface of the polymer composition is irradiated

through a mask.

22. Process according to claim 20, characterized in that the surface of the polymer composition is irradiated with a writing radiation beam.

23. Process according to any one of claims 20-22, characterized in that the radiation load on the surface of the polymer composition is varied locally.

24. Process according to any one of claims 20-23, characterized in that the intensity of the radiation is varied locally.

25. Process according to any one of claims 20-24, characterized in that the surface of the polymer composition is irradiated sequentially with radiation of differing intensity.

26. Process according to any one of claims 20-25, characterized in that the wavelength of the radiation is varied locally.

27. Process according to any one of claims 20-26, characterized in that the surface of the polymer composition is irradiated sequentially with radiation of differing wavelength.

28. Process according to any one of claims 20-27, characterized in that at least one of the radiation sensitive components in the polymer composition is wholly or partially bleached during the irradiation.

29. Process according to claim 28, characterized in that the polymer composition is irradiated with such a radiation load that after the irradiation at least one of the radiation sensitive components shows no absorption any more in the visible range.

30. Process according to any one of claims 20-29, characterized in that the polymer composition is irradiated with such a radiation load that during the irradiation of the polymer composition the surface is foamed at the place of the irradiation.

31. Process according to any one of claims 20-30, characterized in that the polymer composition is irradiated with such a radiation load that at least

one of the radiation sensitive components is wholly or partially removed during the irradiation.

32. Process according to any one of claims 20-31, characterized in that the polymer composition is irradiated with such a radiation load that the surface of the polymer composition melts at the place of the irradiation.

33. Moulding comprising a polymer composition according to any one of claims 1-19.

34. Moulding having a surface that is provided with at least one marking which has a colour contrasting with the colour of the non-irradiated surface, which has been obtained by a process according to any one of claims 20-32.

35. Moulding according to claim 34, characterized in that the surface of the moulding has markings of at least two different colours which differ from the colour of the non-irradiated surface.

36. Moulding according to claim 34 or 35, characterized in that the depth of the marking is 0.1-1000 μm, measured from the surface of the moulding.

37. Article comprising a moulding according to any one of claims 33-36.